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(54) Title: SYNERGISTIC HERBICIDAL METHODS AND COMPOSITIONS

(57) Abstract: The present invention provides a method for the synergistic control of undesirable plants such as Polygonum, Kochia, Galeopsis, Gallium, Stelaria, Sinapis, and Avena which comprises applying to the plants or their locus a synergistically effective amount of an aryloxycolinamide herbicide in combination with one or two selected additional herbicidal compounds. Further provided are synergistic herbicidal compositions comprising an aryloxycolinamide herbicide and one or two selected additional herbicidal compounds.



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SYNERGISTIC HERBICIDAL METHODS AND COMPOSITIONS

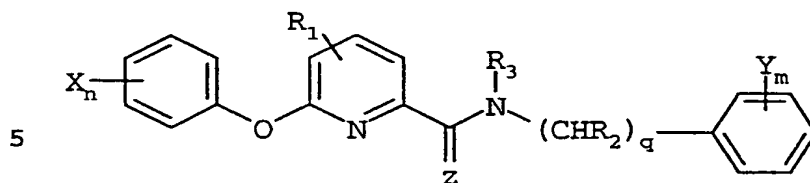
Aryloxypicolinamides such as those described in U.S. 5,294,597
5 demonstrate excellent herbicidal activity, in particular against
broadleaf weeds in cereal crops. However, said aryloxypicolina-
mides, when used as the sole active ingredient, do not always
achieve effective control of the full spectrum of weed species
encountered in commercial agronomic practice at application rates
10 required for acceptable crop safety. Such gaps in the spectrum of
control can often be remedied by co-treatment with another
herbicide known to be effective against the relevant weed
species. It has been disclosed (U.S. 5,674,807) that selected
combinations of aryloxypicolinamides produce not merely the ex-
15 pected additive effect, but may exhibit a significant synergistic
effect (i.e., the combination shows a much higher level of acti-
vity than that which could be predicted from that of the indivi-
dual components). This synergistic effect enables a greater mar-
gin of safety for the crop species. However, the disclosure is
20 limited to two-way combinations of aryloxypicolinamides and mem-
bers of selected known chemical classes which do not include her-
bicidal partners in the imidazolinone, cyclohexanedione, aryloxy-
phenoxypropionic acid, or pyridinecarboxylic acid classes. Moreo-
ver, although the phenoxyacetic acid chemical class is disclosed,
25 2,4-dichlorophenoxyacetic acid (2,4-D), its esters and salts are
not specifically exemplified.

Therefore it is an object of this invention to provide
synergistic, crop-selective herbicidal combinations with broad-
30 spectrum weed control.

It is another object of this invention to provide herbicidal com-
positions useful for the synergistic control of a broad-spectrum
of weeds in the presence of a crop.

35

Although aryloxypicolinamide compounds demonstrate excellent her-
bicidal activity, when applied alone they do not always achieve
the desired spectrum of weed control at rates required for accep-
table crop safety. Surprisingly, it has now been found that a
40 two-way combination comprising an aryloxypicolinamide compound of
formula I



I

10

wherein

Z represents an oxygen or sulfur atom;

15

R_1 represents a hydrogen or halogen atom or an alkyl or haloalkyl group;

R_2 represents a hydrogen or an alkyl group;

20

q is 0 or 1;

R_3 represents a hydrogen or an alkyl or alkenyl group; the or each group X independently represents a

25

halogen atom or an optionally substituted alkyl or alkoxy group, preferably a haloalkyl group, or an alkenyloxy, cyano, carboxy, alkoxycarbonyl, (alkylthio)carbonyl, alkylcarbonyl, amido, alkylamido, nitro, alkylthio, haloalkylthio, alkenylthio, alkynylthio, alkylsulphonyl, alkylsulphonyl, alkyloxyminoalkyl or alkenyloximinoalkyl group;

30

n is 0 or an integer from 1 to 5;

35

the or each group Y independently represents a halogen atom or an alkyl, nitro, cyano, haloalkyl, alkoxy or haloalkoxy group; and

m is 0 or an integer from 1 to 5

40

or one of its environmentally compatible salts;

plus a second herbicide selected from 2,4-dichlorophenoxyacetic acid (2,4-D) or one of its environmentally compatible esters or salts, an imidazolinone, a cyclohexanedione, an aryloxyphenoxypropionic acid, or a pyridinecarboxylic acid herbicide demonstrates a synergistic herbicidal effect. Further, unexpectedly, a se-

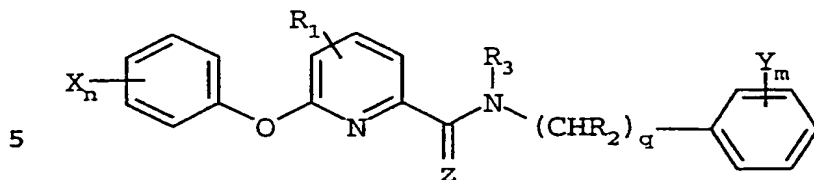
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lected three-way combination comprising an aryloxypicolinamide compound of formula I and 2,4-D or one of its environmentally compatible esters or salts; and a third herbicide selected from the group consisting of an imidazolinone, a cyclohexanedione, and
5 an aryloxyphenoxypropionic acid herbicide produces a significant synergistic effect. Advantageously, the synergistic two-way and three-way combinations of the invention allow for lower application rates of said aryloxypicolinamide with concomittant increased spectrum of weed control. Moreover, the synergistic
10 herbicidal methods and compositions of the invention allow for effective resistance management.

The present invention provides a method for the synergistic control of undesirable plants such as Polygonum, Kochia, Galeopsis,
15 Galium, Stelaria, Sinapis, and Avena which comprises applying to the locus of said plants or to the foliage or stems of said plants a synergistically effective amount of a two-way combination comprising an aryloxypicolinamide compound of formula I plus a second herbicide selected from 2,4-D or one of its environmen-
20 tally compatible esters or salts, an imidazolinone, a cyclohexanedione, an aryloxyphenoxypropionic acid, or a pyridinecarboxylic acid herbicide. The present invention also provides a method for the synergistic control of undesirable plants which comprises applying to the locus of said plants a synergistically effective
25 amount of a three-way combination comprising an aryloxypicolinamide compound of formula I, 2,4-D or one of its environmentally compatible esters or salts, and a third herbicide selected from the group consisting of an imidazolinone, a cyclohexanedione, or an aryloxyphenoxypropionate herbicide.

30 The present invention also provides a synergistic herbicidal composition which comprises an agriculturally acceptable carrier and a synergistically effective amount of a two-way combination of an aryloxypicolinamide compound of formula I plus a second herbicide
35 selected from 2,4-D or one of its environmentally compatible esters or salts, an imidazolinone, a cyclohexanedione, an aryloxyphenoxypropionic acid, or a pyridinecarboxylic acid herbicide; or a three-way combination of an aryloxypicolinamide compound of formula I, 2,4-D or one of its environmentally compatible esters
40 or salts, and a third herbicide selected from the group consisting of an imidazolinone, a cyclohexanedione, and an aryloxyphenoxypropionate herbicide.

Aryloxypicolinamides of formula I



I

10

wherein Z, R₁, R₂, R₃, X, n, Y and m are defined herein above and methods for their preparation are described in U.S. 5,294,597.

Said aryloxypicolinamides demonstrate excellent herbicidal activity, in particular against broadleaf weeds in cereal crops. However, said aryloxypicolinamides when used as the sole active ingredient do not always achieve effective control of the full spectrum of weed species encountered in commercial agronomic practice, in conjunction with reliable selectivity for the crop species.

20

Surprisingly, it has now been found that a two-way combination of an aryloxypicolinamide of formula I and a second herbicide selected from 2,4-D or one of its environmentally compatible esters or salts, an imidazolinone, a cyclohexanedione, an aryloxyphenoxypropionic acid, or a pyridinecarboxylic acid herbicide provides synergistic control of troublesome weeds such as *Polygonum*, *Kochia*, *Galeopsis*, *Galium*, *Stelaria*, *Sinapis*, and *Avena*. Also, surprisingly, a three-way combination of an aryloxypicolinamide of formula I and 2,4-D or one of its environmentally compatible esters or salts plus a third herbicidal compound selected from the group consisting of an imidazolinone, a cyclohexanedione, and an aryloxyphenoxypropionic acid herbicide provides synergistic weed control. That is, the application of the two-way or three-way combinations of the invention gives a mutual reinforcing action such that the application rates of the individual herbicidal components can be reduced and still the same herbicidal effect is achieved or, alternatively, the application of the combination of herbicidal components demonstrates a greater herbicidal effect than expected from the effect of the application of the individual herbicidal components when applied singly at the rate at which they are present in the combination (synergistic effect).

The aryloxypicolinamides of formula I may exist in the form of their environmentally compatible salts. Suitable salts are, in general, the salts of those cations, or the acid addition salts

of those acids, whose cations, or anions, respectively, do not adversely affect the herbicidal action of the active ingredients.

- Suitable cations are, in particular, ions of the alkali metals, preferably lithium, sodium and potassium, of the alkaline earth metals, preferably calcium and magnesium, and of the transition metals, preferably manganese, copper, zinc and iron, and also ammonium, it being possible in this case, if desired, for one to four hydrogen atoms to be replaced by C₁-C₄-alkyl, hydroxy-C₁-C₄-alkyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, hydroxy-C₁-C₄-alkoxy-C₁-C₄-alkyl, phenyl or benzyl, preferably ammonium, dimethylammonium, diisopropylammonium, tetramethylammonium, tetrabutylammonium, 2-(2-hydroxyeth-1-oxy)eth-1-yl ammonium, di(2-hydroxyeth-1-yl)ammonium, trimethylbenzylammonium, furthermore phosphonium ions, sulfonium ions, preferably tri(C₁-C₄-alkyl)sulfonium and sulfoxonium ions, preferably, tri(C₁-C₄-alkyl)sulfoxonium.
- Anions of suitable acid addition salts are mainly chloride, bromide, fluoride, hydrogen sulfate, sulfate, dihydrogen phosphate, hydrogen phosphate, nitrate, hydrogen carbonate, carbonate, hexafluorosilicate, hexafluorophosphate, benzoate and the anions of C₁-C₄-alkanoic acids, preferably formate, acetate, propionate and butyrate.

- In the specification and claims, the term 2,4-D designates 2,4-dichlorophoxyacetic acid. 2,4-D may also exist in the form of its environmentally compatible esters or salts.
- Suitable salts are, in general, the salts of those cations, which do not adversely affect the herbicidal action of the active ingredients.

- Suitable cations are, in particular, ions of the alkali metals, preferably lithium, sodium and potassium, of the alkaline earth metals, preferably calcium or magnesium, and of the transition metals, preferably manganese, copper, zinc and iron, and also ammonium, it being possible in this case if desired, for one to four hydrogen atoms to be replaced by C₁-C₄-alkyl, hydroxy-C₁-C₄-alkyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, hydroxy-C₁-C₄-alkoxy-C₁-C₄-alkyl, phenyl or benzyl, preferably ammonium, dimethylammonium, diisopropylammonium, (2-hydroxy-eth-1-yl)ammonium, di(2-hydroxy-eth-1-yl)ammonium or tri(2-hydroxy-eth-1-yl)ammonium,

Especially suitable cations are sodium, dimethylammonium, di(2-hydroxy-ethyl)ammonium and tri(2-hydroxy-ethyl)ammonium.

- 5 Suitable esters of 2,4-D are the C₁-C₈-alkyl esters, for example the methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl,
- 10 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1-ethyl-1-methylpropyl, 1-ethyl-3-methylpropyl, heptyl, 5-methyl-1-hexyl, octyl, 6-methyl-1-heptyl,
- 15 2-ethyl-1-hexyl or 4-ethyl-1-hexyl esters, or the C₁-C₄-alkoxy-C₁-C₄-alkyl esters for example the methoxymethyl, ethoxymethyl, propoxymethyl, (1-methylethoxy)methyl, butoxymethyl, (1-methylpropoxy)methyl, (2-methylpropoxy)methyl, (1,1-dimethylethoxy)methyl, 2-(methoxy)ethyl, 2-(ethoxy)ethyl,
- 20 2-(propoxy)ethyl, 2-(1-methylethoxy)ethyl, 2-(butoxy)ethyl, 2-(1-methylpropoxy)ethyl, 2-(2-methylpropoxy)ethyl, 2-(1,1-dimethylethoxy)ethyl, 2-(methoxy)propyl, 2-(ethoxy)propyl, 2-(propoxy)propyl, 2-(1-methylethoxy)propyl, 2-(butoxy)propyl, 2-(1-methylpropoxy)propyl, 2-(2-methylpropoxy)propyl,
- 25 2-(1,1-dimethylethoxy)propyl, 3-(methoxy)propyl, 3-(ethoxy)propyl, 3-(propoxy)propyl, 3-(1-methylethoxy)propyl, 3-(butoxy)propyl, 3-(1-methylpropoxy)propyl, 3-(2-methylpropoxy)propyl, 3-(1,1-dimethylethoxy)propyl, 2-(methoxy)butyl, 2-(ethoxy)butyl, 2-(propoxy)butyl, 2-(1-methylethoxy)butyl,
- 30 2-(butoxy)butyl, 2-(1-methylpropoxy)butyl, 2-(2-methylpropoxy)butyl, 2-(1,1-dimethylethoxy)butyl, 3-(methoxy)butyl, 3-(ethoxy)butyl, 3-(propoxy)butyl, 3-(methylethoxy)butyl, 3-(butoxy)butyl, 3-(1-methylpropoxy)butyl, 3-(2-methylpropoxy)butyl, 3-(1,1-dimethylethoxy)butyl, 4-(methoxy)butyl,
- 35 4-(ethoxy)butyl, 4-(propoxy)butyl, 4-(1-methylethoxy)butyl, 4-(butoxy)butyl, 4-(1-methylpropoxy)butyl, 4-(2-methylpropoxy)butyl or 4-(1,1-dimethylethoxy)butyl esters;

Especially suitable esters are the 1-methyl-1-ethyl, butyl,

- 40 6-methyl-1-heptyl, 2-ethyl-1-hexyl or 2-butoxy-1-ethyl esters.

Examples of an imidazolinone herbicide suitable for use in the methods and compositions of the invention include imazapyr, imazethapyr, imazapic, imazaquin, imazamox, imazamethabenz methyl,

- 45 imazamethapyr or the like or one of its environmentally compatible salts, preferably imazamethabenz methyl. Suitable salts are in general, the salts of those anions which do not adversely af-

fect the herbicidal action of the active ingredient. They are similar to those listed for the compounds of formula I.

A cyclohexanedione herbicide suitable for use in the methods and compositions of the invention include sethoxydim, clethodim, alloxydim, tralkoxydim, cycloxydim, butroxydin, clefoxydim, cloprooxydim, tepraloxym or the like, or one of its environmentally compatible salts preferably tralkoxydim. Suitable salts are in general the salts of those cations which do not adversely affect the herbicidal action of the active ingredient. They are similar to those listed for the compounds of formula I.

Exemplary of aryloxyphenoxypropionate herbicides suitable for use in the inventive methods and compositions are fluazifop-p-butyl, fenoxaprop-ethyl, fenoxaprop-p-ethyl, quizalofop-p-terfuryl, quizalofop-p, haloxyfop-methyl, clodinafop-propargyl, isoxapurifop, cyhalofop butyl, fenthionprop, propaquizafop, quizalafop-ethyl, quizalafop-P-ethyl or the like, or one of its environmentally compatible salts or esters, preferably fenoxaprop-p-ethyl. Suitable salts or esters are similar to those listed for 2,4-D.

A pyridinecarboxylic acid herbicide such as picloran, clopyralid, or the like, preferably clopyralid, is suitable for use in the two-way combination of the invention. Also salts thereof may be used. Suitable salts are similar to those listed for 2,4-D.

In the specification and claims, the term alkyl (alone or in combination) represents a C₁-C₆-alkyl group, especially a C₁-C₄-alkyl group; the term alkoxy (alone or in combination) represents a C₁-C₆-alkoxy group, especially a C₁-C₄-alkoxy group; the term alkenyl (alone or in combination) represents a C₃-C₆-alkenyl group, especially a C₃-C₄-alkenyl group; the term alkynyl represents a C₃-C₆-alkynyl group, especially a C₃-C₄-alkynyl group.

Preferred synergistic combinations of the invention are those two-way or three-way combinations containing a formula I aryloxy-picolinamide wherein

Z is oxygen;

R₁ is hydrogen;

q is 0;

R₃ is hydrogen;

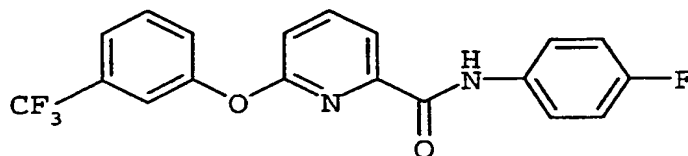
X is haloalkyl; and

Y is hydrogen or fluorine.

5 Especially those two-way or three-way combinations containing a formula I aryloxypicolinamide wherein $n=1$ and X is linked in meta-position to the phenyl radical (with regard to the oxygen bridge).

10 More preferred synergistic two-way and three-way combinations are those wherein the formula I compound is N-(4-fluorophenyl)-6-[3-trifluoromethylphenoxy]-2-pyridine carboxamide illustrated below, and hereinafter designated, picolinafen.

15



20

picolinafen

Preferred second herbicides for the two-way combinations of the invention are 2,4-D, imazamethabenz methyl, tralkoxydim, fenoxa-
25 prop-p-ethyl, and clopyralid.

Another preferred embodiment of the invention are those two-way combinations wherein the second herbicide is 2,4-D or one of its environmentally compatible esters or salt, especially 2,4-D.

30

Another preferred embodiment of the invention are those two-way combinations wherein the second Herbicide is selected from the group consisting of an imidazolinone herbicide, a cyclohexanedi-
one herbicide and a pyridinecarboxylic acid herbicide. Especially

35 the second herbicide is imazamethabenz methyl, tralkoxydim or clopyralid.

Another preferred embodiment of the invention are those two-way combinations wherein the second herbicide is an aryoxyphenoxy-
40 propionate herbicide. Especially the second herbicide is fenoxa-prop-p-ethyl.

Preferred third herbicides for the three-way combination of the invention are imazamethabenz methyl, tralkoxydim or fenoxaprop-
45 p-ethyl.

Another preferred embodiment of the invention are those three-way combinations wherein the third herbicide is selected from the group consisting of an imidazolinone herbicide and a cyclohexanedione herbicide.

5

Especially the third herbicide is imazamethabenz methyl or tralkoxydim.

Another preferred embodiment of the invention are those three-way
10 combinations wherein the third herbicide is an aryloxyphenoxypropionate herbicide. Especially the second herbicide is fenoxaprop-p-ethyl.

In actual practice, the combination of the invention may be
15 applied simultaneously (as a tank mix or a premix), separately or sequentially.

Thus, in accordance with the method of invention a synergistically effective amount of a two-way combination of aryloxypicolinamide and a second herbicide selected from 2,4-D, or one of its environmentally compatible salts or esters, an imidazolinone, a cyclohexanedione, an aryloxyphenoxypropionic acid, or a pyridine-carboxylic acid herbicide; or a synergistically effective amount of a three-way combination of an aryloxypicolinamide, 2,4-D, or
25 one of its environmentally compatible salts or esters and a third herbicide selected from an imidazolinone, a cyclohexanedione, or an aryloxyphenoxypropionate is applied to the locus, foliage or stems of undesirable plants, particularly plants selected from the genera Polygonum, Kochia, Galeopsis, Galium, Stelaria, Sinapis, and Avena, optionally in the presence of a crop, preferably
30 a cereal crop such as wheat, barley, rice, corn, rye or the like.

The synergistically effective amount of the two- and three-way combinations described above may vary according to prevailing
35 conditions such as the particular second and third component present, weed pressure, application timing, weather conditions, soil conditions, mode of application, topographical character, target crop species and the like.

40 Preferred two-way combinations of the invention are those wherein the weight/weight ratio of the aryloxypicolinamide of formula I to the second compound is about:

aryloxypicolinamide:2,4 D (or its salts or ester), 1:1 to 1:25;

45

aryloxypicolinamide:imidazolinone herbicide, 1:1 to 1:35;

10

aryloxypicolinamide:cyclohexenedione herbicide, 1:1 to 1:20;

aryloxypicolinamide:aryloxyphenoxypropionate herbicide, 1:1 to 1:10;

5

aryloxypicalinamide:pyridicarboxylic acid herbicide, 1:1 to 1:15.

More preferred two-way combinations of the invention are those wherein the weight/weight ratio of picolinafen to the second component is about:

10

picolinafen:2,4-D, 1:1 to 1:25;

picolinafen:imazethabenz methyl, 1:1 to 1:35;

15

picolinafen:tralkoxydim, 1:1 to 1:20;

picolinafen:fenoxaprop-p-ethyl, 1:1 to 1:10; or

20

picolinafen:clopyralid, 1:1 to 1:15.

Preferred three-way combinations of the invention are those wherein the weight/weight ratio of the aryloxypicolinamide of formula I to 2,4-D (or its salts or esters) to third component is about:

25

aryloxypicolinamide: 2,4 D (or its salts or esters):
imidazolinone herbicide, 1:1:1 to 1:35:25;

30 aryloxypicolinamide: 2,4 D (or its salts or esters): cyclohexanedione herbicide; 1:1:1 to 1:20:25;

aryloxypicolinamide: 2,4 D (or its salts or esters): aryloxyphenoxypropionate herbicide, 1:1:1 to 1:10:25.

35

More preferred three-way combinations of the invention are those wherein the weight/weight/weight ratio of picolinafen to 2,4-D to third component is about:

40

picolinafen:2,4-D:imazamethabenz methyl, 1:1:1 to 1:35:25;

picolinafen:2,4-D:tralkoxydim, 1:1:1 to 1:20:25; or

picolinafen:2,4-D:fenoxaprop-p-ethyl, 1:1:1 to 1:10:25.

45

The present invention also provides a synergistic herbicidal composition comprising an agriculturally acceptable carrier and a synergistically effective amount of a two-way combination of an aryloxycolinamide of formula I and a second herbicidal compound
5 selected from the group consisting of 2,4-D, or one of its environmentally compatible salts or esters an imidazolinone herbicide, a cyclohexanedione herbicide, an aryloxyphenoxypropionic acid herbicide and a pyridinecarboxylic acid herbicide. The present invention further provides a synergistic herbicidal composition which comprises an agriculturally acceptable carrier and
10 a synergistically effective amount of a three-way combination of an aryloxycolinamide compound of formula I, 2,4-D, or one of its environmentally compatible salts or esters and a third herbicidal compound selected from the group consisting of an
15 imidazolinone herbicide, a cyclohexanedione herbicide, and an aryloxyphenoxypropionate herbicide.

The agriculturally acceptable carrier may be a solid or a liquid, preferably a liquid, more preferably water. While not required,
20 the combination compositions of the invention may also contain other additives such as fertilizers, inert formulation aids, i.e. surfactants, emulsifiers, defoamers, dyes, extenders or any of the conventional inert ingredients typically employed in herbicidal formulated products.

25 Compositions according to the invention may be formulated in any conventional form, for example in the form of a twin pack, or as an aqueous concentrate, soluble granular, dispersible granular or the like.

30 Preferred two-way combination compositions of the invention are those compositions wherein the aryloxycolinamide compound is picolinafen. Also preferred are those synergistic two-way combination compositions having a second herbicide selected from the
35 group consisting of 2,4-D, imazamethabenz methyl, tralkoxydim, fenoxaprop-p-ethyl and clopyralid. More preferred two-way combination compositions of the invention are those compositions of the invention wherein the weight/weight ratio of picolinafen to second component is about:

- 40 picolinafen:2,4-D, 1:1 to 1:25;
- picolinafen:imazethabenz methyl, 1:1 to 1:35;
- 45 picolinafen:tralkoxydim, 1:1 to 1:20;

12

picolinafen:fenoxaprop-p-ethyl, 1:1 to 1:10; or

picolinafen:clopyralid, 1:1 to 1:15.

5 Preferred three-way combination compositions of the invention are those compositions wherein the picolinamide compound is picolinafen. Also preferred are those synergistic three-way combination compositions having a third herbicide selected from the group consisting of imazamethabenz methyl, tralkoxydim and fenoxaprop-
10 p-ethyl. More preferred three-way combination compositions of the invention are those compositions wherein the weight/weight/weight ratio of picolinafen to 2,4-D to third component is about:

picolinafen:2,4-D:imazamethabenz methyl, 1:1:1 to 1:35:25;

15

picolinafen:2,4-D:tralkoxydim, 1:1:1 to 1:20:25; or

picolinafen:2,4-D:fenoxaprop-p-ethyl, 1:1:1 to 1:10:25.

20 For a more clear understanding of the invention, specific examples thereof are set forth below. These examples are merely illustrative, and are not to be understood as limiting the scope and underlying principles of the invention in any way.

25 In the following examples, synergism for two-way combinations is determined by the Colby method (S.R. Colby, Weeds 1967 (15), 20), i.e. the expected (or predicted) response of the combination is calculated by taking the product of the observed response for each individual component of the combination when applied alone
30 divided by 100 and subtracting this value from the sum of the observed response for each component when applied alone. Synergism of the combination is then determined by comparing the observed response of the combination to the expected (or predicted) response as calculated from the observed responses of each indi-
35 dual component alone. If the observed response of the combination is greater than the expected (or predicted) response then the combination is said to be synergistic and falls within the definition of synergistic effect as previously defined.

40 The foregoing is illustrated mathematically below, wherein a two-way combination, C_2 , is composed of component X plus component Y and Obs. designates the observed response of the combination C_2 .

$$(X + Y) - \frac{XY}{100} = \text{Expected response (Exp.)}$$

5 Synergism \equiv Obs. > Exp.

10 In similar manner for the case of three-way combination, C_3 , is composed of component X plus component Y plus component X and Obs. designates the observed response of the combination C_3 .

$$(X + Y + Z) - \frac{(XY+XZ+YZ)}{100} + \frac{XYZ}{10000} = \text{Exp.}$$

15 Synergism \equiv Obs. > Exp.

In the following examples, crop tolerance ratings are taken periodically throughout the growing season. The first rating is taken one to two weeks after treatment and the final rating is taken just prior to harvest. For all treatments described in the following examples crop tolerance was commercially acceptable, i.e. $\leq 20\%$ injury, on each of the three crops tested. None of the treatments demonstrated commercially unacceptable injury to 25 barley, durum wheat or hard red spring wheat.

EXAMPLE 1

30 Evaluation of the Herbicidal Activity of a Combination of Picolifafen and 2,4-Dichlorophenoxyacetic Acid

Grassy and broadleaved weeds are either seeded perpendicular to the direction of the crop or broadcast in early to mid-May. The crop is seeded after the weed seed. Row width is 18 cm. The seed 35 is drilled in with a Roger's 1.8 m width drill to a depth of 5 cm.

All trials employ standard accepted weed science procedures. Applications are made with a Roger's CO₂-powered shrouded sprayer. 40 Test design is a modified randomized complete block design with four replications. All applications are made post-emergence to the weeds and crop.

The test solutions are prepared by tank-mixing sufficient quantities of aqueous solutions and/or dispersions of the test 45 compounds.

The treated plots are examined at intervals during the growing season and rated for percent control of weeds and crop injury. The data listed is an average of the replicates for that treatment. The Colby method of analysis is used to determine the resultant biological effect of the combination treatment as compared to the biological effect of each component when applied alone. The data are reported in Table I.

As can be seen from the data shown in Table I, application of a combination of picolinafen plus 2,4-D gave significantly greater weed control than that which could be predicted from the weed control resulting from the application of either picolinafen alone or 2,4-D alone.

15 TABLE I

Evaluation of the Herbicidal Activity of a Combination of Picolinafen plus 2,4-D

Weed Species	picolinafen 50g/ha	2,4-D 280g/ha	picolinafen + 2,4-D 50g/ha + 280 g/ha	
	Percent Control		Observed	Expected
<i>Avena fatua</i>	5	2	15	7
<i>Chenopodium album</i>	57	91	97	96
<i>Polygonum convolvulus</i>	54	48	80	76
<i>Galeopsis tetrahit</i>	59	2	70	60
<i>Polygonum</i> (smartweed) spp.	26	53	85	65
<i>Vaccaria pyramidata</i>	63	51	97	82

EXAMPLE 2

Evaluation of the Herbicidal Activity of a Combination of Picolinafen and Imazamethabenz Methyl

Following essentially the same procedure described in Example 1 and employing picolinafen and imazamethabenz methyl, the data shown in Table II are obtained.

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As can be seen from the data in Table II, the application of a combination of picolinafen plus imazamethabenz methyl gives significantly greater weed control than that which could be predicted from the weed control resulting from the application of either picolinafen alone or imazamethabenz methyl alone.

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TABLE II

Evaluation of the Herbicidal Activity of a Combination of Picolinafen plus Imazamethabenz Methyl

Weed Species	picolinafen 50g/ha	imazamethabenz methyl 400g/ha	Percent Control	
			Observed	Expected
<i>Avena fatua</i>	5	88	91	89
<i>Setaria viridis</i>	14	10	42	23
<i>Brassica napus</i> (Imidazolinone tolerant)	65	0	86	65
<i>Chenopodium album</i>	57	18	86	65
<i>Galeopsis tetrahit</i>	59	4	76	61
<i>Galium aparine</i>	28	48	90	63
<i>Polygonum spp.</i>	26	76	84	82
<i>Kochia scoparia</i>	59	31	85	72
<i>Salsola kali</i>	56	9	79	60
<i>Vaccaria pyramida</i>	63	20	77	70

EXAMPLE 3

Evaluation of the Herbicidal Activity of a Combination of Picolinafen and Tralkoxydim

Following essentially the same procedure as described in Example 1 and employing picolinafen and tralkoxydim, the data shown in Table III are obtained

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As can be seen from the data shown on Table III, the application of a combination of picolinafen plus tralkoxydim gives significantly greater weed control than that which could be predicted from the weed control resulting from the application of either
15 picolinafen alone or tralkoxydim alone.

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TABLE III

Evaluation of the Herbicidal Activity of a Combination of Picolinafen plus Tralkoxydim

Weed Species	picolinafen 50g/ha	tralkoxydim 200g/ha	Percent Control	
			Observed	Expected
<i>Avena fatua</i>	5	97	98	97
<i>Sinapis arvensis</i>	78	0	94	78
<i>Brassica napus</i>	70	0	95	70
<i>Brassica napus</i> (imidazolinone tolerant)	65	0	92	65
<i>Amaranthus retroflexus</i>	90	1	98	90
<i>Chenopodium album</i>	57	0	93	57
<i>Polygonum convolvulus</i>	54	0	87	54
<i>Vaccaria pyramidalata</i>	63	0	86	63

EXAMPLE 4

Evaluation of the Herbicidal Activity of a Combination of Picolinafen and Fenoxaprop-p-ethyl

Following essentially the same procedure as described in Example 1 and employing picolinafen and fenoxaprop-p-ethyl, the data shown in Table IV are obtained.

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As can be seen from the data shown on Table IV, the application of a combination of picolinafen plus fenoxaprop-p-ethyl gives significantly greater weed control than that which could be predicted from the weed control resulting from the application of either picolinafen alone or fenoxaprop-p-ethyl alone.

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TABLE IV

Evaluation of the Herbicidal Activity of a Combination of Picolinafen plus Fenoxaprop-p-ethyl

Weed Species	picolinafen 50g/ha	fenoxaprop- p-ethyl 72g/ha	picolinafen + fenoxa- prop-p-ethyl 50g/ha + 72 g/ha	
	Percent Control		Observed	Expected
<i>Sinapis arvensis</i>	78	0	96	78
<i>Setaria viridis</i>	14	98	99	98
<i>Brassica napus</i>	70	0	97	70
<i>Brassica napus</i> (imidazolinone tolerant)	65	0	97	65
<i>Amaranthus retroflexus</i>	90	9	94	91
<i>Chenopodium album</i>	57	0	95	57
<i>Polygonum convolvulus</i>	54	0	74	54
<i>Vaccaria pyramidalata</i>	63	0	71	63

EXAMPLE 5

Evaluation of the Herbicidal Activity of a Combination of Picolinalafen and Clopyralid

Following essentially the same procedure as in Example 1 and employing picolinalafen and clopyralid, the data shown in Table V are obtained.

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As can be seen from the data shown on Table IV the application of a combination of picolinalafen plus clopyralid gives significantly greater weed control than that which could be predicted from the weed control resulting from the application of either picolinalafen
15 alone or clopyralid alone.

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TABLE V

Evaluation of the Herbicidal Activity of a Combination of Picolinafen plus Clopyralid

Weed Species	picolinafen 50g/ha	clopyralid 150g/ha	picolinafen + clopyralid 50g/ha + 150g/ha	
	Percent Control	Control	Observed	Expected
<i>Sinapis arvensis</i>	78	16	87	82
<i>Brassica napus</i>	70	12	78	74
<i>Brassica napus</i> (imidazolinone tolerant)	65	8	85	68
<i>Chenopodium album</i>	57	51	83	79
<i>Stellaria media</i>	64	10	70	68
<i>Galium aparine</i>	28	0	30	28

EXAMPLE 6

Evaluation of the Herbicidal Activity of a Combination of Picolinafen, Imazamethabenz Methyl and 2,4-D

Following essentially the same procedure as described in Example 1 and employing picolinafen, 2,4-D and imazamethabenz methyl, the data shown in Table VI are obtained.

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As can be seen from the data on Table VI, the application of a combination of picolinafen, 2,4-D and imazamethabenz methyl gives significantly greater weed control than that which could be predicted from the weed control resulting from the application of
15 picolinafen alone, 2,4-D alone or imazamethabenz methyl alone.

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TABLE VI

Evaluation of the Herbicidal Activity of a Combination of Picolinafen, 2,4-D and Imazamethabenz Methyl

Weed Species	picolinafen 50g/ha	imazamethabenz methyl 400 g/ha	2,4-D 280g/ha	picolinafen + 2,4-D + imazametha- benz methyl 50g/ha + 280g/ha + 400g/ha	Expected
	Percent Control			Observed	
<i>Avena fatua</i>	5	88	2	91	89
<i>Setaria viridis</i>	14	10	0	49	23
<i>Stellaria media</i>	64	8	10	86	70
<i>Galeopsis tetrahit</i>	59	4	2	82	61
<i>Galium aparine</i>	28	48	43	94	79
<i>Polygonum spp.</i>	26	76	53	99	92
<i>Kochia scoparia</i>	59	31	52	93	86
<i>Salsola kali</i>	56	9	35	97	74
<i>Vaccaria pyramidalata</i>	63	20	51	93	85

EXAMPLE 7

Evaluation of the Herbicidal Activity of a Combination of Picolinfen, Tralkoxydim and 2,4-D

Following essentially the same procedure as described in Example 1 and employing picolinfen, 2,4-D, and tralkoxydim, the data shown in Table VII are obtained.

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As can be seen from the data on Table VII, the application of a combination of picolinfen, 2,4-D and tralkoxydim gives significantly greater weed control than that which could be predicted from the weed control resulting from the application of picolinfen alone, 2,4-D alone or tralkoxydim alone.

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TABLE VII

Evaluation of the Herbicidal Activity of a Combination of Picolinafen plus 2,4-D and Tralkoxydim

Weed Species	picolinafen 50g/ha	tralkoxydim 200g/ha	2,4-D 280g/ha	picolinafen + 2,4-D + tralkoxydim 50g/ha + 200g/ha + 280g/ha	Expected
	Percent Control			Observed	
<i>Avena fatua</i>	5	97	2	98	97
<i>Sinapis arvensis</i>	78	0	92	99	98
<i>Brassica napus</i>	70	0	93	100	98
<i>Brassica napus</i> (imidazolinone tolerant)	65	0	94	100	98
<i>Chenopodium album</i>	57	0	91	98	96
<i>Polygonum convolvulus</i>	54	0	48	90	76
<i>Vaccaria pyramidalata</i>	63	0	51	90	82

EXAMPLE 8

Evaluation of the Herbicidal Activity of a Combination of Picolinafen, 2,4-D and Fenoxaprop-p-ethyl

Following essentially the same procedure as described in Example 1 and employing picolinafen, 2,4-D and fenoxaprop-p-ethyl, the data shown in Table VIII are obtained.

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As can be seen from the data shown in Table VIII, the application of a combination of picolinafen, 2,4-D and fenoxaprop-p-ethyl gives significantly greater weed control than that which could be predicted from the weed control resulting from the application of picolinafen alone, or 2,4-D alone or fenoxaprop-p-ethyl alone.

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TABLE VIII

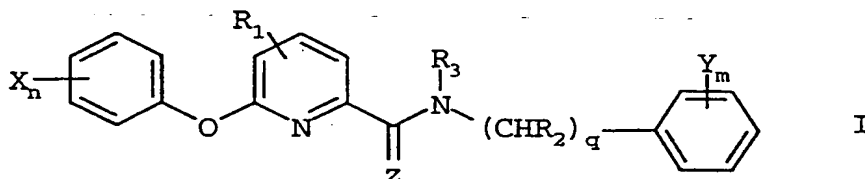
Evaluation of the Herbicidal Activity of a Combination of

Picolinafen, plus 2,4-D and Fenoxaprop-p-ethyl

Weed Species	picolinafen 50g/ha	fenoxaprop- p-ethyl 72 g/ha	2,4-D 280g/ha	picolinafen + 2,4-D + fenoxa- prop-p-ethyl 50g/ha + 280g/ha + 72g/ha	Expected
	Percent Control			Observed	
<i>Brassica napus</i>	70	0	93	100	98
<i>Brassica napus</i> (imidazolinone tolerant)	65	0	94	100	98
<i>Chenopodium album</i>	57	0	91	97	96
<i>Polygonum convolvulus</i>	54	0	48	93	76
<i>Vaccaria pyramidalata</i>	63	0	51	96	82

We claim:

1. A synergistic herbicidal composition which comprises an agriculturally acceptable carrier and a synergistically effective amount of a two-way combination of an aryloxypicolinamide of formula I



wherein

- Z represents an oxygen or sulfur atom;
- R₁ represents a hydrogen or halogen atom or an alkyl or haloalkyl group;
- R₂ represents a hydrogen or an alkyl group;
- q is 0 or 1;
- R₃ represents a hydrogen or an alkyl or alkenyl group;
- the or each group X independently represents a halogen atom or an optionally substituted alkyl or alkoxy group, preferably a haloalkyl group, or an alkenyloxy, cyano, carboxy, alkoxycarbonyl, (alkylthio)carbonyl, alkylcarbonyl, amido, alkylamido, nitro, alkylthio, haloalkylthio, alkenylthio, alkynylthio, alkylsulphanyl, alkylsulphonyl, alkyloxyminoalkyl or alkenyloximinoalkyl group;
- n is 0 or an integer from 1 to 5;
- the or each group Y independently represents a halogen atom or an alkyl, nitro, cyano, haloalkyl, alkoxy or haloalkoxy group; and
- m is 0 or an integer from 1 to 5
- or one of its environmentally compatible salts;

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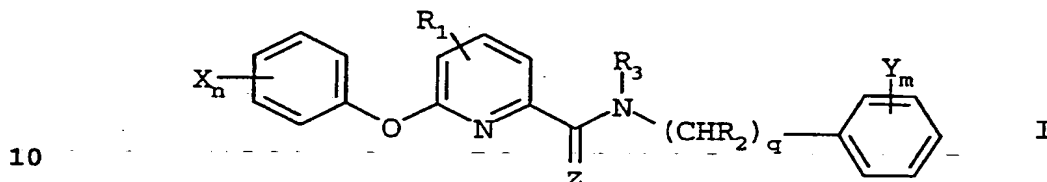
and a second herbicide selected from the group consisting of 2,4-D or one its environmentally compatible salts or esters; an imidazolinone herbicide, a cyclohexanedione herbicide, an aryloxyphenoxypropionate herbicide and a pyridinecarboxylic acid herbicide.

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2. The composition according to claim 1 having a formula I aryloxypicolinamide wherein
- 10 Z is oxygen;
- R₁ is hydrogen;
- q is 0;
- 15 R₃ is hydrogen;
- X is haloalkyl; and
- 20 Y is hydrogen or fluorine.
3. The composition according to claim 2 wherein said formula I aryloxypicolinamide is picolinafen.
- 25 4. The composition according to claim 1 wherein the second herbicide is 2,4-D or one of its environmentally compatible esters or salts.
5. The composition according claim 1 wherein the second herbicide is selected from the group consisting of an imidazolinone herbicide, a cyclohexanedione herbicide and a pyridinecarboxylic acid herbicide.
- 30 6. The composition according claim 5 wherein the second herbicide is imazamethabenz methyl, tralkoxydim or clopyralid.
- 35 7. The composition according claim 1 wherein the second herbicide is an aryloxyphenoxypropionate herbicide.
- 40 8. The composition according to claim 7 wherein the second herbicide is fenoxaprop-p-ethyl.
9. The composition according to claims 4 to 8 wherein said formula I aryloxypicolinamide is picolinafen.
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10. A synergistic herbicidal composition which comprises an agriculturally acceptable carrier and a synergistically effective amount of a three-way combination consisting essentially of: an aryloxypicolinamide of formula I

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wherein

- 15 Z represents an oxygen or sulfur atom;
- R₁ represents a hydrogen or halogen atom or an alkyl or haloalkyl group;
- 20 R₂ represents a hydrogen or an alkyl group;
- q is 0 or 1;
- R₃ represents a hydrogen or an alkyl or alkenyl group;
- 25 the or each group X independently represents a halogen atom or an optionally substituted alkyl or alkoxy group, preferably a haloalkyl group, or an alkenyloxy, cyano, carboxy, alkoxycarbonyl, (alkylthio)carbonyl, alkylcarbonyl, amido, 30 alkylamido, nitro, alkylthio, haloalkylthio, alkenylthio, alkynylthio, alkylsulphiny, alkylsulphonyl, alkyloxyiminoalkyl or alkenyloximinoalkyl group;
- n is 0 or an integer from 1 to 5;
- 35 the or each group Y independently represents a halogen atom or an alkyl, nitro, cyano, haloalkyl, alkoxy or haloalkoxy group; and
- 40 m is 0 or an integer from 1 to 5
- or one of its environmentally compatible salts;

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2,4-D or one its environmentally compatible esters or salts and a third herbicide selected from the group consisting of an imidazolinone herbicide, a cyclohexanedione herbicide and an aryloxyphenoxypropionic acid herbicide.

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11. The composition according to claim 10 having a formula I aryloxypicolinamide wherein

10 Z is oxygen;
 R₁ is hydrogen;
 q is 0;
15 R₃ is hydrogen;
 X is haloalkyl; and
 Y is hydrogen or fluorine.

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12. The composition according to claim 11 wherein said formula I aryloxypicolinamide is picolinafen.
13. The composition according to claim 10 wherein the third
25 herbicide is selected from the group consisting of an imidazolinone herbicide and a cyclohexandione herbicide.
14. The composition according to claim 13 wherein the third
 herbicide is imazamethabenz methyl or tralkoxydim.
- 30 15. The composition according to claim 10 wherein the third herbicide is an aryloxyphenoxypropionate herbicide.
16. The composition according to claim 15 wherein the third
35 herbicide is fenoxaprop-p-ethyl.
17. The composition according to claims 13 to 16 wherein said formula I aryloxypicolinamide is picolinafen.
- 40 18. A method for the synergistic control of undesirable plants, which comprises applying to the locus of said plants or to the foliage or stems of said plants a synergistically effective amount of the compositions as claimed in any of claims 1 to 17.

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